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# Rhenium monoselenide: An investigation by density functional theory

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The lattice parameters and the relative stability of the hypothetical material ReSe have been calculated within the LDA approximation in the NaCl, NiAs, and zincblende structures. The zincblende phase appears to remain metallic even when possible strong Coulomb correlations between Re  $5d$  electrons are taken into account by the introduction of a Hubbard  $U$  term.

Spin-polarized calculations predict a non-magnetic phase for  $U$  up to 7 eV. Calculations of the phonon dispersion of zincblende ReSe point to an instability with respect to a tetragonal distortion and this raises the interesting possibility that it may also be possible to obtain ReSe experimentally in the PbO (FeSe) structure.

**1 Introduction** The drive to combine magnetic and semiconducting properties within the same material has revealed a wide range of fascinating and fundamental spin-dependent physics in III–V, II–VI [1, 2] and, most recently, van der Waals layered semiconductors such as MoS<sub>2</sub>. However, at present, it is unclear whether many of the aims of spintronics can be realized, and what the most promising materials may be for practical applications [3, 4]. It is therefore a priority to explore ideas for novel materials that may address the technological challenges and may also present interesting new physics.

Here, we consider the hypothetical zincblende compound ReSe, asking whether it may be expected to behave in an analogous manner to zincblende MnSe, since atomic Re and Mn appear somewhat similar in having electronic configurations [Xe]  $5d^5 6s^2$  and [Ar]  $3d^5 4s^2$ , respectively. Experimentally, MnSe has been studied extensively in its most stable structures, which are the cubic rocksalt NaCl (room temperature) and hexagonal NiAs ( $T < 266$  K) phases [5, 6], whilst metastable MnSe layers of thickness less than about 5 nm can be grown in the zincblende (ZB) phase by molecular beam epitaxy (MBE) [7–9]. Finally, nanocrystalline MnSe can be obtained in the hexagonal wurtzite phase, where the effects of nanocrystal morphology stabilize the hexagonal structure [10–12]. In the bulk phases, the manganese  $3d^5$  electronic configuration generates

a large magnetic moment per Mn<sup>2+</sup> ion with dominant nearest-neighbor  $d$ – $p$ – $d$  exchange that leads to antiferromagnetic ordering with reported Néel temperatures from 120 to 150 K [8, 13, 14] (AF2 ordering, NaCl structure) and 70 to 110 K (AF3 ordering, ZB structure) [7, 8]. ZB MnSe has attracted particular attention because it is a direct gap semiconductor with a lattice parameter compatible with ZnSe-based hetero-structures and GaAs substrates. First-principles calculations based on density functional theory (DFT) at various levels of approximation have been reasonably successful in modeling the structural, electronic, and magnetic properties of MnSe (and many similar transition metal chalcogenides) though the limitations of DFT mean that this is a challenging task [15]. By contrast, there are no reports of the observation of rhenium monoselenide nor any computational studies of ReSe to date.

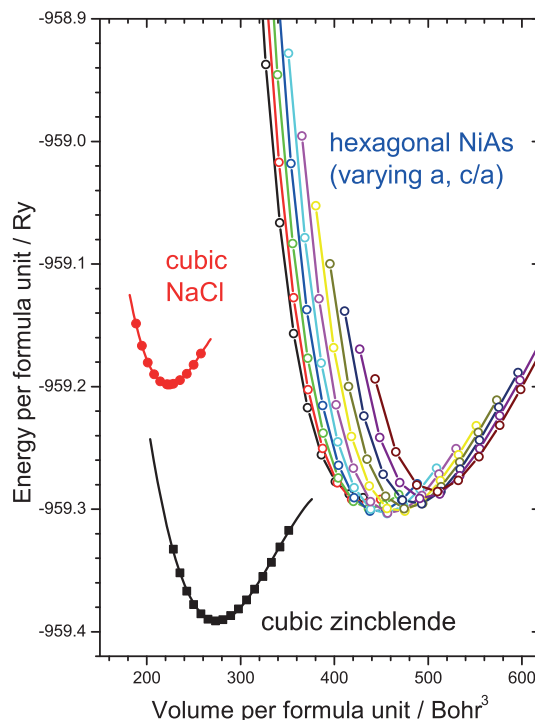
The most stable known selenide of rhenium is the layered transition metal dichalcogenide ReSe<sub>2</sub> [16, 17] but it is likely to be possible to obtain metastable zincblende ReSe layers by non-equilibrium growth techniques such as molecular beam epitaxy, as has been demonstrated for numerous other transition metal chalcogenides including (for example) MnSe [7–9, 18, 19], CrSe [20], and MnTe [21]. Furthermore, HgSe, the end-member of the  $5d$ -selenide series to which ReSe would belong, occurs naturally in the zincblende structure with a lattice parameter of 6.085 Å and can be grown by

MBE on GaSb substrates [22]. To attempt MBE growth of a previously unknown material, guidance concerning the likely ZB lattice parameter is useful in order to identify appropriate epitaxial substrates and so we have carried out first-principles calculations of some basic properties of ZB ReSe. Here, we do not attempt an exploration of all possible crystal structures for ReSe, but focus on the behavior expected of zincblende ReSe, with comparison only to the other structures known to be adopted by MnSe.

**2 Calculation details** First-principles calculations were carried out within density functional theory (DFT) using the projector-augmented wave method [23] with a plane wave basis as implemented within Quantum Espresso (QE) [24]. The scalar relativistic pseudopotentials used for Re and Se were generated from the library distributed with the QE code [25] and were extensively tested, in particular by calculations of lattice dynamics and band structure for the layered semiconductor ReSe<sub>2</sub> where very good agreement was found with experimental data [17]. The use of both the local density approximation (LDA) and generalized gradient approximation (GGA) was investigated; here, for brevity, we only present results obtained within the LDA. Kinetic energy and charge density cutoffs of 70 and 700 Ry, respectively, were used, and  $12 \times 12 \times 12$  and  $12 \times 12 \times 8$  Monkhorst–Pack [26] meshes were used for Brillouin zone integration for cubic (ZB, NaCl) and hexagonal (NiAs) structures, respectively.

The ZB phonon dispersion was calculated after minimization of the interatomic forces. The density functional perturbation theory (DFPT) method for lattice dynamics was used as implemented within QE [27]. To investigate electronic band structures and spin-dependent densities of states, the local spin density approximation (LSDA) was used with collinear magnetism only and without the inclusion of spin-orbit coupling. The effects of inclusion of a Hubbard  $U$  term to account for possible correlations of the localized Re  $d$ -electrons (LDA+ $U$ ) [28] were also investigated, though this work is still in progress. At this level of approximation, we (and others) already obtain plausible predictions for the lattice properties and magnetic states of the ZB phases of, for example, CrSe (half-metallic ferromagnetic) [29, 30], though MnSe presents difficulties [15].

**3 Results** Figure 1 shows the total energy as a function of volume per formula unit for ReSe in the three crystal structures relevant to MnSe: cubic rocksalt (RS) and ZB, and hexagonal NiAs, from non-spin-polarized calculations. For the NiAs structure, the lattice parameters  $a$  and  $c$  were varied independently, giving the set of curves shown on Fig. 1 and these parameters were then relaxed to locate the minimum energy more precisely. Of these three configurations, the ZB phase has the lowest energy; for the possible epitaxial growth of ZB ReSe, this is an encouraging result, though it should be interpreted very cautiously. For example, it is known that GGA and GGA +  $U$  predictions of the relative stability of rocksalt and ZB MnSe disagree with experiment [15] and so our preliminary LDA results (Table 1) require further explo-



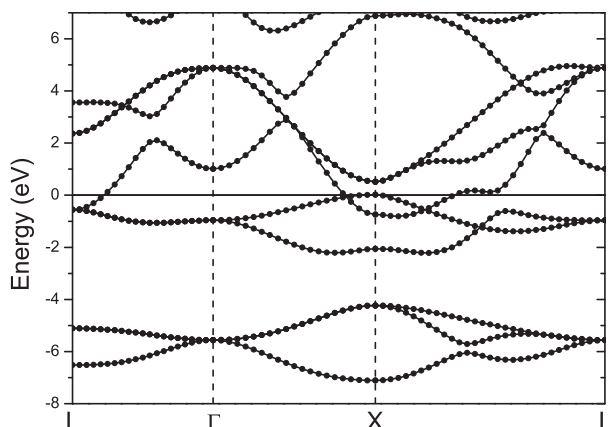
**Figure 1** Total energy versus volume per formula unit for ReSe in three crystal structures. Points are calculated and solid lines are fits (NaCl, ZB) or guides to the eye (NiAs). For hexagonal NiAs, each curve in the left-to-right sequence (black to brown) corresponds to a constant value of  $a$  from 3.70 (left) to 4.23 (right) in steps of 0.053, with  $c/a$  varying from 1.00 to 1.45 in steps of 0.05 along each curve; the minimum energy position was found by relaxation of the cell dimensions and atomic coordinates.

ration. However, the energy difference between ZB and RS structures in our case is particularly large (2.7 eV per formula unit) compared to the case of MnSe, where calculations predict that the ZB structure is only marginally more stable than RS (about 0.2 eV per formula unit). Since we aim to assist future MBE growth, we also show in Table 1 the value of  $a$  given by the GGA, which typically yields an over-estimate by 2–3% and so sets a plausible upper bound; overall, our predicted range of  $a$  lies between those of GaAs and GaP substrates.

Focusing now on the ZB phase, electronic band structure calculations show metallic behavior, as indicated by Fig. 2. This is expected in the absence of any Hubbard  $U$  term that might relocate the partially filled Re  $5d$  orbitals away from the Fermi energy [28]. Turning to Fig. 3, the bottom panel shows the spin-polarized density of states (DOS) for this band

**Table 1** Predicted lattice parameters of ReSe (LDA).

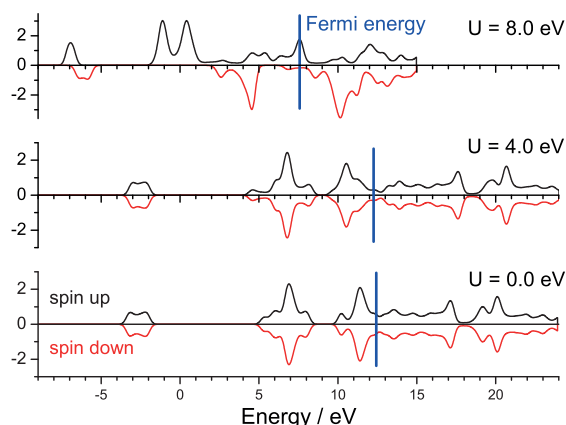
structure	$a$ (Å)	$c$ (Å)	$a$ (GGA)
rocksalt (NaCl)	5.0896		
hexagonal (NiAs)	3.9343	5.0153	
zincblende	5.4521		5.5706



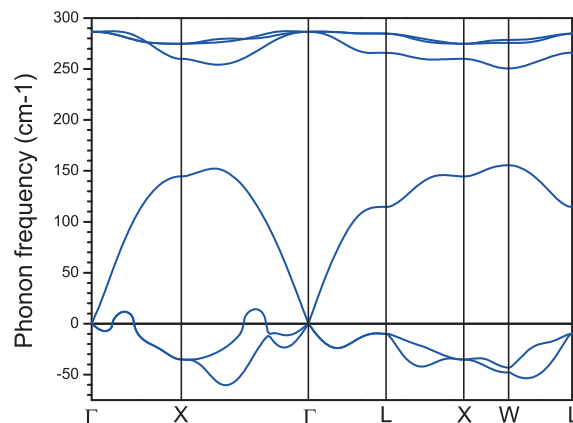
**Figure 2** Electronic band structure of zinc blende ReSe calculated in the non-spin-polarized LDA approximation without a Hubbard  $U$  term; the Fermi energy is taken as the zero of energy.

structure, showing that a non-magnetic state is predicted (this holds independent of whether ferromagnetic or antiferromagnetic starting points are used in the calculation). As a preliminary exploration of what may be obtained for a ZB phase in the LDA +  $U$  approximation, we also show spin-polarized densities of states in Fig. 3 for  $U = 4.0$  and  $8.0$  eV (at each  $U$ , the equilibrium lattice parameter was re-determined; there is a  $\sim 15\%$  increase in  $a$  at  $U = 8.0$  eV). When  $U \geq 7.0$  eV, a ferromagnetic state with a magnetization of  $\sim 5 \mu_B$  per Re atom is predicted; calculations in 1 eV steps show the transition to the ferromagnetic state occurs for  $U$  between 6 and 7 eV. Work is in progress to explore possible antiferromagnetic states and to determine a value of  $U$  by linear response methods [31], but it is interesting to note that a metallic state results even for this large value of  $U$ .

Before embarking on a detailed study of LDA +  $U$  or GGA +  $U$  methods applied to zincblende ReSe, the stability of the ZB structure with respect to structures other than those adopted by MnSe should be tested. In particular, there is a



**Figure 3** Predicted spin-polarized densities of states of zinc blende ReSe (via LDA+ $U$ ) for Hubbard  $U$  values of 0, 4 and 8 eV from bottom to top. The Fermi energy in each case is indicated by the vertical blue line.



**Figure 4** Predicted phonon dispersion for metallic zincblende ReSe (LDA,  $U = 0$ ); negative frequencies represent imaginary solutions of the dynamical matrix and imply structural instability.

variety of tetragonal phases that could be considered. As a first step, we have therefore calculated the phonon dispersion of the ZB phase, as shown in Fig. 4. It is clear that imaginary solutions to the dynamical matrix arise for phonon wavevectors away from the  $\Gamma$  point (plotted as negative in Fig. 4). Tests confirm these results are not due to poor relaxation of the starting structures or insufficient convergence of the phonon calculations (and the results are independent of the choice of LDA or GGA). They therefore indicate an instability with respect to distortion into a different structure, for which a possibility (not yet considered) is the tetragonal PbO structure adopted by the spin-density wave material and high temperature superconductor FeSe [32], which is of great current interest. It is thus a priority for future work to address the PbO as well as the ZB structure; a full study of ReSe in the PbO structure is under way and we note that early results within the LDA show that the PbO structure is indeed more stable than the ZB phase. This, of course, does not imply that epitaxial growth of a metastable ZB phase could not still be successful.

**4 Conclusions** The relative stability and the lattice parameters of three phases of the hypothetical material ReSe have been calculated within the LDA approximation; the crystal structures considered were based on those adopted in nature by MnSe. We find, however, that the behavior expected of ReSe is different to MnSe and, so far, do not find a semiconducting or Mott insulator zincblende phase even when possible strong Coulomb correlations between Re  $5d$  electrons are taken into account by the introduction of a Hubbard  $U$  term. The zincblende phase is found to be the most stable of the three considered but calculations of the phonon dispersion point to an instability with respect to a tetragonal distortion and this raises the interesting possibility that it may also be possible to produce ReSe in the PbO (FeSe) structure. Several directions for future work are indicated and it is clear that these new phases of ReSe should be exciting targets for epitaxial growth.

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